

SCIENCE FOR CERAMIC PRODUCTION

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FORMATION OF OPEN MICROPORES IN NANOPOROUS CERAMICS BASED ON ORGANOSILICON POLYMERS

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Micropores in nanoporous ceramics produced by pyrolysis of organosilicon polymers are investigated using BET and mercury porosimetry methods. The poor reproducibility of the obtained micropore structure is interpreted in the context of synergism.

Good service properties, high chemical and thermal resistance, and an extended surface are responsible for the wide application of porous ceramics. Such ceramics at present are used as filters and catalyst carriers, membranes and dust collectors, adsorbents and heat exchangers, and also in biotechnology and in medicine.

One of the methods for producing porous ceramic is using burning-out additives. The pore size in this case is determined by the size of particles of the burning-out additive. To obtain nano-sized pores, one needs a burning-out additive with the respective particle size. Pyrolysis of organometallic polymers is such a method. Nanopores with a narrow size distribution are obtained in this way.

Production of ceramics based on organometallic polymers usually includes molding (casting, extrusion, pressing, fiber drawing, etc.) with subsequent heat treatment at 150 – 250°C to produce a solid thermoreactive polymer and pyrolysis in an inert atmosphere or an atmosphere reacting with the material at 500 – 1500°C. In the course of pyrolysis, the functional organic groups are removed at a temperature of 400 – 800°C, and an amorphous porous inorganic material is formed, which crystallizes at temperatures exceeding 1000 – 1600°C [1].

The breaking-off and removal of organic functional groups leading to the formation of nanometric pores depends on many factors. The formation in pyrolysis of a maximum quantity of nanopores with a narrow size distribution is largely determined by the specific structure of the material formed in the course of the pre-pyrolysis heat treatment [2]. When producing catalysts or sensors, the nonporous material has to have larger pores allowing gases to easily reach the in-

ner parts of the sample. To ensure high strength, the larger pores should have similar sizes and be uniformly distributed in the bulk of the material, i.e., the material should have a bimodal size distribution of pores.

The purpose of the present study is to investigate the possibility of producing a nanoporous material containing sufficiently large micropores that are close in size. The polymer used in the experiments was SR350 (methyl siloxane) in the form of a 43 – 45% ready solution in a xylene isomeric mixture (Baysilone Harz M 120 XB, GE Bayer Silicones GmbH). The catalyst for cross-linking of the polymer was 3,2-aminoethylamine.

Samples containing two types of pores (nanopores and pores with a large diameter) were produced by two methods.

In the first method, the polymer solution was thoroughly mixed with 4 wt.% catalyst, poured into a cylindrical Teflon mold (diameter 26 mm, height 54 mm), held for 5 h at room temperature, and placed in a drying cabinet for pre-pyrolysis treatment, which was carried out in an air atmosphere according to the following program: temperature rise at a rate of 30 K/h up to 200°C, exposure for 2 h, and cooling at a rate of 30 K/h. The pyrolysis was carried out in a flowing nitrogen medium according to the following program: the temperature rising at a rate of 120 K/h up to 500°C, then rising at a rate of 30 K/h to a final temperature of 600°C, exposure at this temperature for 4 h, and cooling (120 K/h).

According to the second method, the polymer solution was mixed as well with 4% catalyst, but unlike the first method, instead of thorough mixing, the mixture was stirred for 2 min with a glass rod. In the course of a 2-h exposure the mixture stratified into two layers, which either were subjected to pre-pyrolysis treatment together in the same mold, or separated and heated in individual Teflon molds. The pre-

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pyrolysis treatment and the pyrolysis were carried out similarly as in the first method, except for having two 2-h exposures at 80 and 140°C during the pre-pyrolysis treatment.

After the pre-pyrolysis treatment, cylindrical samples were obtained having small bubbles and grooves that were preserved after pyrolysis, but the results had poor reproducibility. Each of the experiments mentioned was repeated several times, and the obtained intermediate samples differed in color (from turbid orange to brown) and size of the microbubbles. Some samples had large cavities and ruptures in the lower part, and only some samples had approximately equally distributed bubbles of about equal size.

The reasons for the formation of such structure can be found in the context of synergism, i.e., a science studying the processes of self-organization, stability, and disintegration of structures within systems.

If a polymer is not well mixed with a catalyst, only a part of the polymer chain reacts with the catalyst and, consequently, participates in the polycondensation reaction and becomes cross-linked. The catalyst concentration in these portions of the sample is very high, which provides for a high degree of nonequilibrium of the polycondensation process. The latter, in turn, leads to the formation of a polymer with a disordered structure and, accordingly, with a low density. The low-density polymerized parts of the polymer float on the surface, which outwardly appears as a stratification of the solution into two layers after 2 h exposure at room temperature. The upper layer has a lighter color and is less transparent than the lower one. Later in the course of the pre-pyrolysis treatment, the upper layer prevents removal of gases by developing foam.

Bubbles as well can be formed if the melt viscosity is too high to remove the gases — water or solvent — that are released in heat treatment. This can be accomplished by subjecting the gel-like mixture condensed in air to thermal drying according to an accelerated program without exposures at 80 and 140°C (the first method). Due to the polymerization of the polymer, the released gases are forced to pass through a medium with a high viscosity.

The specific surface area of pyrolyzed samples was measured based on low-temperature nitrogen absorption (BET), and the size distribution of pores in the range of 0.1 – 100 nm in samples was measured by the gas-absorption method (Gemini and ASAP 2000 instruments, respectively). The mercury porosimetry method was used (on a Pascal 140 device for low pressure and a Pascal 440 for high pressure) to determine the size of the pores in the range of 0.001 – 100 μm .

The specific surface area of the upper layer in the samples prepared by the second method was 229 m^2/g . The shape of the adsorption isotherm is typical of an adsorbent with extremely small pores. The average pore diameter lies within the limits of 1 – 2 nm. The porosity in the range of 0.001 – 100 μm is 10.26%, and the average pore diameter is 0.004 μm . The specific surface area of the samples prepared by the first method was equal to 41 m^2/g .

After studying samples prepared with a catalyst additive, the conclusion was made that a system based on organosilicon resin M 120 XB and the catalyst is unstable and extremely sensitive to all kinds of effects (the chain cross-linking temperature, the exposure duration, the program of the pre-pyrolysis treatment, etc.). Significant modifications occur in the properties of the end product under slight variations of the conditions of material preparation, and it is difficult to predict in which direction the system will evolve.

According to the contemporary notions of synergism, all natural processes are irreversible and nonequilibrium. Systems that are understood as space volumes separated by a real or imaginary boundary from the surrounding space (the environment) evolve in the sequence stability – instability – stability or, in other words, attractor – bifurcation – attractor [3, 4].

The processes in open systems are determined by the degree of their nonequilibrium, i.e., the intensity of exchange between the material and the environment. When a system is in a stable state, a negative feedback is present in it. According to the Le Chatelier – Brown principle, a system creates structures impeding an external influence. When a system is in an unstable state, a positive feedback is present, and the system acquires enhanced sensitivity to internal fluctuations and to external disturbances. An unstable state of the system can be a bifurcation. A bifurcation is a manifestation of the probabilistic aspect of matter [3].

In the case of micropore formation in a nanoporous material, we are dealing with a multistable system, whose stable states significantly differ in their properties [5]. To improve the reproducibility of the structure of the material produced within the range of this unstable state, it is necessary to exercise controlling effects exceeding the noise level upon the system. The controlling effects can be internal, i.e., existing inside the system, or external, i.e., acting from the ambient medium [6, 7].

An attempt was made to stabilize the system by introducing an internal controlling effect represented by a filler at a filler : mixture (the mixture is the polymer solution + 4% catalyst) ratio equal to 1 : 3. The filler was prepared from an identical mixture dried at room temperature in the form of a thin layer for 5 days and then milled in a planetary mill. This experiment resulted in a complete loss of all microbubbles in the end product. The gases emitted under pre-pyrolysis heat treatment are presumably removed along the boundaries separating the filler particles from the polymer and do not form bubbles.

In forming bubbles according to the second method, i.e., under poor mixing of the catalyst with the polymer solution and a subsequent stratification of the mixture, the upper layer of the polymer contained many cavities. It was impossible to control the reproducibility of the structure of these pores in the conditions of the experiment due to the high degree of the process nonequilibrium. The experiments performed to simplify the process, for instance, the use of a well homogenized mixture initially containing an excessive amount of the cata-

lyst, demonstrated that a variation of the catalyst content from 2 to 6 wt.% had no effect on the result. In introducing more than 10% catalyst, the system becomes so nonequilibrium that all samples disintegrate in the course of pre-pyrolysis heat treatment.

Thus, the nonequilibrium state of the system reached either by too fast heating of a well mixed mixtures or by poor mixing with the catalyst (creation of local excesses of the catalyst) has a dual role. On the one hand, the nonequilibrium state of the system results in it accumulating an excessive energy input in pre-pyrolysis heat treatment due to the formation of microbubbles. On the other hand, the nonequilibrium state of the system in these conditions does not allow for stable reproducible results. It is necessary to search for controlling effects on the system and to regulate the degree of nonequilibrium of the process in order to eliminate the multistability, whose stable states have highly different properties.

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